# Diorganogallium complexes containing tripodal Schiff bases: synthesis and structure of [N{$Me_2GaO(C_6H_4)CH=N–CH_2–CH_2$-}$_3$]

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Treatment of triorganogallium etherates with tripodal Schiff bases in benzene gave complexes of composition [N{$R_2GaO(C_6H_3X)CH=N–CH_2–CH_2$–}$_3$] (R = Me, Et; X = H, OMe) in nearly quantitative yield. The molecular structure of [N{$Me_2GaO(C_6H_4)CH=N–CH_2–CH_2$-}$_3$] revealed that there are two different types of molecules in the crystal lattice each containing three distorted tetrahedral gallium atoms.

**Keywords:** organogallium, Schiff base, crystal structure

Organo-gallium/indium compounds with anionic oxo-ligands have attracted considerable attention recently due to their structural diversity,[1] their potential application as catalysts[2] or as molecular precursors for the preparation of metal oxide thin films,[3,4] and their interesting photo-physical properties.[5,6] Most investigations have dealt with the compounds of composition, "$R_2ML$" (R = alkyl; M = Ga or In; L= anionic oxo-ligand). These compounds have been isolated using either simple anionic ligands (*e.g.*, alcoholates, phenolates or carboxylates)[7] or internally functionalised/bidentate anionic ligand precursors (*e.g.*, aminoalcohols, β-diketones, salicyldehyde, oxazolines, *etc.*).[8–11] The resulting complexes exist as mono-, bi- or tri-nuclear species both in the solid state and in solution and several of them have a centro-symmetric "$M_2(\mu\text{-}O)_2$" core.

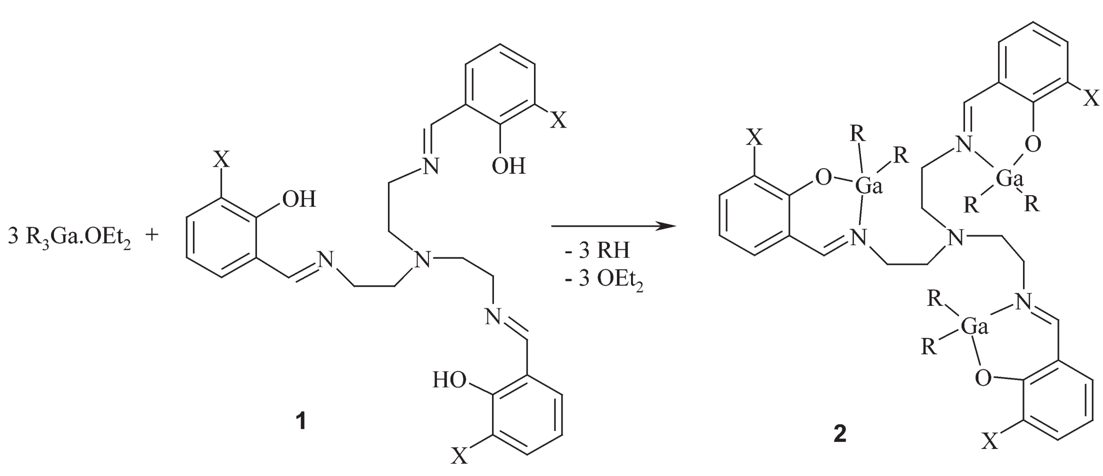
Recently binuclear diorgano-gallium/indium complexes based on salen-type Schiff bases have been described.[12–14] These complexes, devoid of the "$M_2(\mu\text{-}O)_2$" core, show polymorphism and are also emissive in solution at room temperature.[12] Another interesting family of ligands is the "saltren" type of tripodal Schiff bases (**1**). These potentially heptadentate, tri-anionic ligands facilitate the formation of discrete complexes by encapsulation of trivalent metal ions. In lanthanide complexes, ([LnL]) (Ln = lanthanide ion; $LH_3$ = saltren), the ligand enforces a seven coordinate geometry around the lanthanide ion,[15–18] whereas hexa-coordination is preferred by trivalent transition metal ions.[19,20] The divalent metal ions (*e.g.*, Zn, Cd, Ni), however, form trinuclear complexes [$M_3L_2$], with these ligands.[21–23]

We have examined reactions with saltren ligand (**1**) with the hope of isolating a new structural motif. The results of this work are reported here.

## Results and discussion

The ligands [**1**, X = H, (**1a**)] and [**1**, X = OMe, (**1b**)] (Scheme 1) have been prepared by condensation reaction between an aromatic aldehyde and tris(2-aminoethyl)amine (supplementary material). A metathetical reaction between trialkylgallium· diethylether adduct and **1a** or **1b** in 3:1 stoichiometry in benzene solution gave the diorganogallium complexes, [N{$R_2GaO(C_6H_3X)CH=N–CH_2–CH_2$–}$_3$] (**2**) (Scheme 1).

The IR spectra of ligands and diorganogallium complexes showed a characteristic imine CH=N absorption band at ~1630 $cm^{-1}$ which was slightly blue-shifted on complexation. A strong intensity band in the region 540–580 $cm^{-1}$ may be assigned to υ Ga–C stretching. The high field resonances in the $^1H$ (δ ~ –0.25 ppm) and $^{13}C$ (δ ~ –6.5 ppm) NMR spectra of dimethylgallium complexes are in accordance with the chemical shifts shown by the $Me_2Ga$ fragment. In the $^{13}C$ NMR spectra of the complexes, the $–CH_2N=$ carbon resonance is shielded (1.1 ppm) while the –CH=N– signal is deshielded (~ 4 ppm) with reference to the corresponding resonances for free ligands, suggesting coordination of the azomethine nitrogen atom to




| R | X | |
|---|---|---|
| Me | H | **2a** |
| Et | H | **2b** |
| Me | OMe | **2c** |
| Et | OMe | **2d** |

**Scheme 1**

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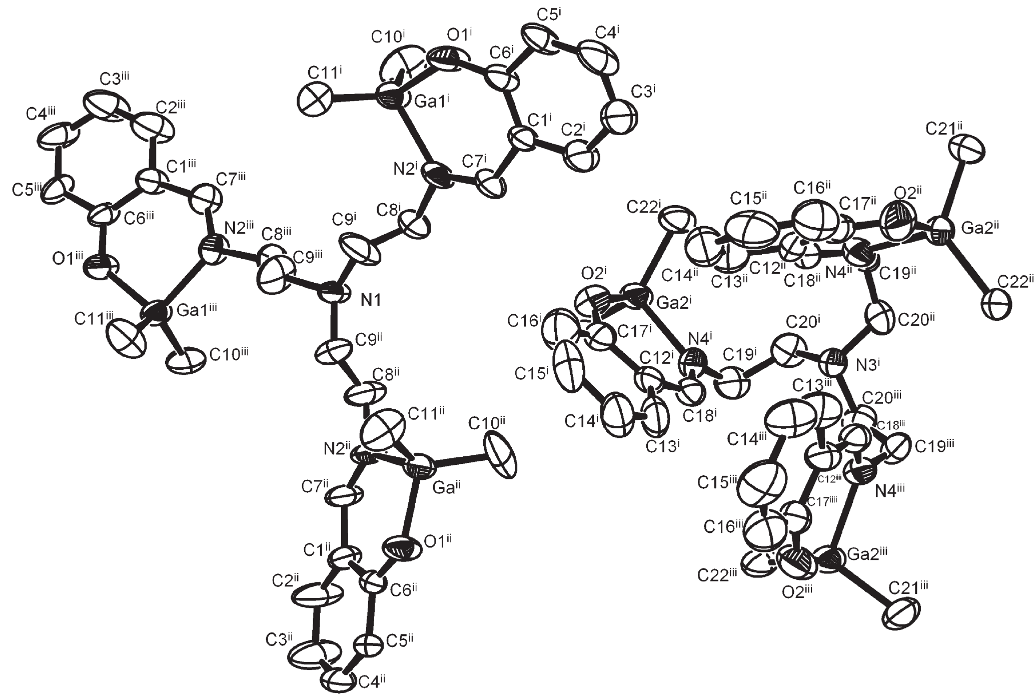


(a) (b)

**Fig. 1** ORTEP drawing of **2a** with atomic numbering scheme (ellipsoids drawn with 25% probability).

gallium. However, in the [1]H NMR spectra of ligands and complexes the $=NCH_2$, $–CH_2N–$ and –CH=N– proton resonances appeared at δ ~2.85, ~3.52 and ~7.82 ppm, respectively and are little influenced by complexation.

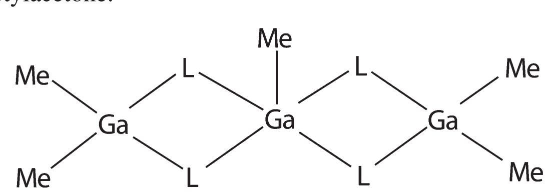
Yellow crystals of $[N\{Me_2GaO(C_6H_4)CH{=}N–CH_2–CH_2–\}_3]$ **(2a)** were obtained by recrystallising the complex from dichloromethane. The molecular structure of **2a** is shown in Fig. 1 and the selected geometric parameters are collected in Table 1. There are two molecules in the crystal lattice differing in the conformation around the central nitrogen atom, one having a planar structure (**a**) [C9–N1–C9 angle = 111.3(7)°] and another having a closed structure (**b**) [C20–N3–C20 angle = 108.7(6)°]. Various bond lengths and angles involving gallium in the two molecules differ slightly. Each closed molecule (**b**) is surrounded by three planar molecules (**a**) through secondary weak H-contacts (2.28–2.60Å) (see CCDC 760549 http://www.ccdc.cam.ac.uk/conts/retrieving.html). The planes formed by connecting N1 atoms are parallel and separated from each other on either side without any interaction. The inter-planar distance on one side is 5.540Å while on other side it is 8.635 Å (Fig. 2). The short contacts with the neighbouring molecules within each plane seem to be responsible for the formation of an infinite sheet. Recently complexes containing ligands derived from *tris*-(2-aminoethyl)amine have been prepared. The central nitrogen atom in these complexes adopts three different conformations, *viz*, trigonal planar, pyramidal with the nitrogen pointing either towards the metal atom ("N in") or pointing away from the metal atom ("N out").[24]

**Table 1** Selected geometric parameters (Å, °) for (**2a**)

| Molecule (a) | | Molecule (b) | |
|---|---|---|---|
| Ga1–O1 | 1.838 (6) | Ga2–O2 | 1.889 (8) |
| Ga1–C10 | 1.918 (10) | Ga2–C21 | 1.964 (9) |
| Ga1–C11 | 1.950 (9) | Ga2–C22 | 1.968 (9) |
| Ga1–N2 | 2.013 (7) | Ga2–N4 | 2.033 (8) |
| N2–C7 | 1.278 (9) | N4–C18 | 1.245 (11) |
| N2–C8 | 1.479 (10) | N4–C19 | 1.464 (10) |
| C6–O1 | 1.304 (9) | C17–O2 | 1.302 (13) |
| C10–Ga1–C11 | 125.8 (5) | C21–Ga2–C22 | 123.9 (4) |
| C10–Ga1–N2 | 104.3 (4) | C21–Ga2–N4 | 106.9 (4) |
| C10–Ga1–O1 | 110.0 (5) | C21–Ga2–O2 | 108.7 (4) |
| C11–Ga1–N2 | 112.6 (4) | C22–Ga2–N4 | 111.2 (3) |
| C11–Ga1–O1 | 106.3 (5) | C22–Ga2–O2 | 108.3 (4) |
| O1–Ga1–N2 | 93.0 (3) | O2–Ga2–N4 | 93.6 (4) |
| C6–O1–Ga1 | 131.6 (6) | C17–O2–Ga2 | 129.9 (9) |
| C7–N2–Ga1 | 121.9 (6) | C18–N4–Ga2 | 121.9 (8) |
| C8–N2–Ga1 | 120.0 (5) | C19–N4–Ga2 | 118.8 (7) |
| $C9^i$–N1–$C9^{ii}$ | 111.3 (7) | $C20^i$–N3–$C20^{ii}$ | 108.7 (6) |
| $C9^i$–N1–$C9^{iii}$ | 111.3 (7) | $C20^i$–N3–$C20^{iii}$ | 108.7 (6) |
| $C9^{ii}$–N1–$C9^{iii}$ | 111.3 (7) | $C20^{ii}$–N3–$C20^{iii}$ | 108.7 (6) |

Each molecule comprises three distorted tetrahedral dimethylgallium fragments included in six-membered chelate rings. The coordination environment around each gallium atom is defined by two methyl groups, the phenolic oxygen atom and the nitrogen of the azomethine linkage. The Ga–C, Ga–O and Ga–N distances are well within the ranges reported for diorganogallium compounds (*e.g.*, $[Me_2Ga(OC_9H_6N)]_2$,[25] $[(Me_2GaOC_6H_4CH{=}N)_2CH_2CH_2]$,[14] and $[\{Me_2Ga(OCH_2CH_2CH_2NH_2)\}_2]$[9]).

The complexes (**2**) reported here represent the first example of trinuclear gallium complexes devoid of the "Ga(μ-O)" core, although only few trinuclear gallium complexes with bridging ligands have been reported in the literature. In $[Me_5Ga_3\{OC(Me_2)CH_2C(Me_2)O\}_2]$ two alkoxide ligands bridge two terminal $Me_2Ga$ four-coordinated units and a central five-coordinated MeGa unit.[26] A similar structural motif (**3**) has been identified for the product isolated from the reaction between trialkylgallium and the bis(thiosemicarbazone) of acetylacetone.[27]




(**3**)

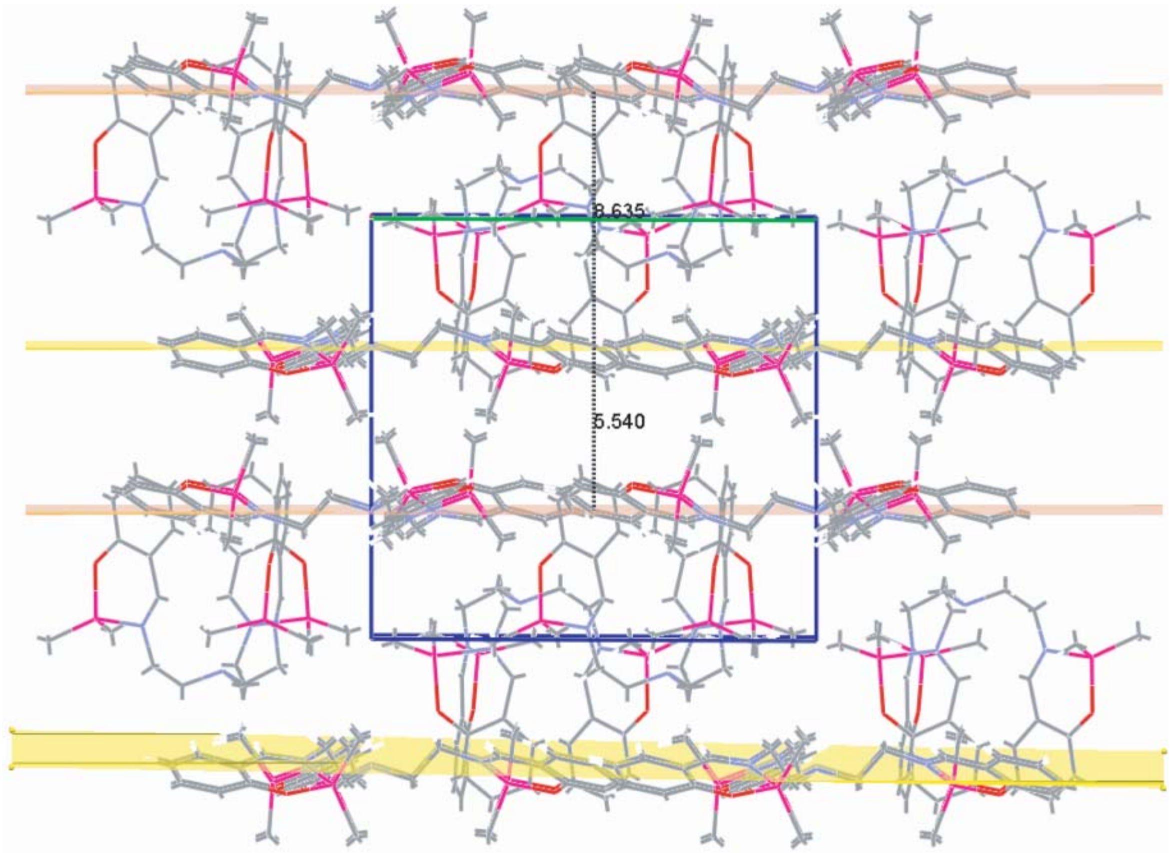



**Fig. 2** Plane packing of **2a** along the a-axis.

The photoluminescent properties of aluminum, gallium and indium complexes with chelating O∩N ligands have received considerable attention recently due to their potential use as organic light-emitting diodes (OLEDs)[5,6] with $AlQ_3$ being the extensively studied compound.[28] Mono- and bi-nuclear gallium complexes derived from ligands other than 8-hydroxyquinolate have been shown to be emissive in solution.[5,29] The trinuclear gallium complexes described here are emissive at room temperature. The benzene solution of these complexes on excitation at ~400 nm showed an emission (Fig. 3) at 455 nm and 505 nm for complexes containing the trianions of **1a** and **1b**, respectively.

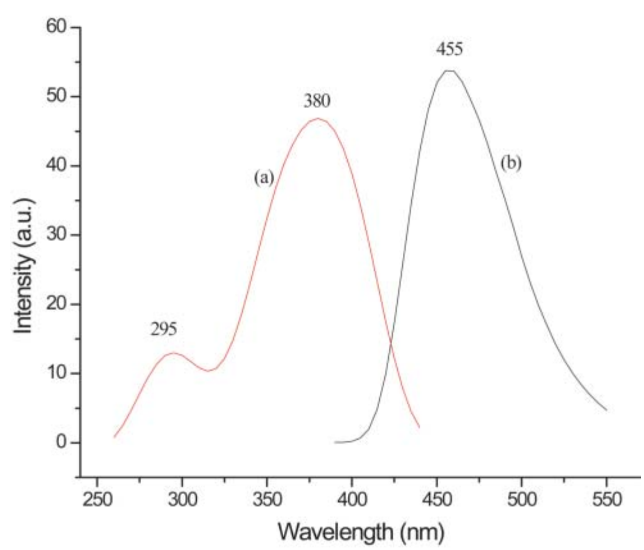



**Fig. 3** Excitation and emission spectra of **2a**.

## Experimental

All experiments involving organo-gallium compounds were carried out under anhydrous conditions under a nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard methods. The trialkyl gallium ether adducts, $R_3Ga.OEt_2$ (R = Me, Et) were prepared from gallium–magnesium alloy and alkyl iodide in diethyl ether.[12] The ether contents in each preparation were evaluated by $^1$H NMR integration.

IR spectra were recorded as KBr pellets on a 4100 Type A FT/IR spectrometer. The NMR spectra were recorded on a Bruker Avance-II 300 spectrometer in 5 mm tubes as $CDCl_3$ solutions. Chemical shifts were referenced to the internal chloroform peak (δ 7.26 and 77.0 ppm for $^1$H and $^{13}C\{^1H\}$, respectively). Electronic spectra were recorded in benzene or dichloromethane on a Chemito Spectroscan UV-double beam spectrophotometer. Emission spectra were recorded in deoxygenated solvents on a Hitachi F-4010 Fluorescence spectrophotometer. Quantum yield measurements were performed in deoxygenated solvents on an Edinburgh Instruments FLSP-920T spectrophotometer.

*[N{Me₂GaO(C₆H₄)CH=N–CH₂–CH₂-}₃]* (**2a**): To a benzene solution (25 mL) of trimethylgallium etherate, (2.93 g containing 13.6 mmol $Me_3Ga$), was added a solution of tris{(2-hydroxybenzylidene)aminoethyl}amine (2.08 g, 4.53 mmol) with stirring, which continued for 3 h. The solvent was evaporated under a reduced pressure to give a yellow crystalline solid (2.05 g, 98%) which was recrystallised from dichloromethane–hexane as a yellow crystalline solid, m.p. 134 °C. Anal. Calcd for $C_{33}H_{45}Ga_3N_4O_3$: C, 52.5; H, 6.0; N, 7.4; Ga, 27.7. Found: C, 52.3; H, 6.0; N, 6.8; Ga, 27.5%. IR in cm$^{-1}$: 1630 (νC=N), 580 (νGa–C), 566 (νGa–O). $^1$H NMR ($CDCl_3$) δ: –0.27 (s, $Me_2Ga$); 2.82 (t, 6.0 Hz $NCH_2$–); 3.51 (t, 6.7 Hz); 6.56 (s); 6.83 (d, 7.5 Hz); 7.31–7.40, (m); 7.74 (s, N=CH–). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: –6.7 (s, $Me_2Ga$); 54.8 (s, $NCH_2$); 56.5 (s, $CH_2$); 116.8, 117.9, 122.4, 135.2, 136.5, 166.8, 170.7 (CH=N).

*[N{Et₂GaO(C₆H₄)CH=N–CH₂–CH₂-}₃]* (**2b**): To a benzene solution (25 mL) of triethylgallium etherate, (1.14 g containing 3.0 mmol $Et_3Ga$), was added a solution of tris{(2-hydroxybenzylidene)aminoet

hyl}amine (0.46 g, 1.0 mmol) with stirring, which continued for 3 h. The solvent was evaporated under a reduced pressure to give a yellow paste (0.78 g, 97%). Anal. Calcd for $C_{39}H_{57}Ga_3N_4O_3$: C, 55.8; H, 6.8; N, 6.7; Ga, 24.9. Found: C, 54.2; H, 6.8; N, 5.7; Ga, 24.9%. IR in $cm^{-1}$: 1625 (νC=N), 540 (νGa–C), 510 (νGa–O).). $^1H$ NMR ($CDCl_3$) δ: 0.43 (q, 7.9 Hz $GaCH_2$–, 12H); 1.06 (t, 8 Hz, $GaCH_2Me$, 18H); 2.87 (t, 6.5 Hz $NCH_2$–, 6H); 3.52 (t, 6.5 Hz, 6H); 6.60 (t, 7.5 Hz, 3H); 6.81 (d, 7.8 Hz, 3H ); 6.84 (d, 8.5 Hz, 3H); 7.33 (s, 3H); 7.88 (s, N=CH–, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 3.8 (s, $GaCH_2$); 9.7 (s, $GaCH_2Me$); 54.7 (s, $NCH_2$); 56.5 (s, $CH_2$); 116.4, 117.9, 122.4, 135.2, 136.6, 167.3, 170.7 (CH=N).

*[N{Me₂GaO(C₆H₃OMe-3)CH=N–CH₂–CH₂-}₃]* (**2c**): To a benzene solution (25 mL) of trimethylgallium etherate, (1.95 g containing, 3.57 mmol $Me_3Ga$), was added a solution of tris{(2-hydroxy-3-metho xybenzylidene)aminoethyl}amine (653 mg, 1.19 mmol) with stirring, which continued for 3 h. The solvent was evaporated under a reduced pressure to give a yellow solid (982 mg, 97%), m.p. 55 $^0$C. Anal. Calcd for $C_{36}H_{51}Ga_3N_4O_6$: C, 51.2; H, 6.1; N, 6.6; Ga, 24.7. Found: C, 50.8; H, 6.0; N, 6.5; Ga, 24.5%. IR in $cm^{-1}$: 1628 (υ C=N); 520 (υ Ga–C). $^1H$ NMR ($CDCl_3$) δ: –0.25 (s, $Me_2Ga$); 2.84 (t, 6.3 Hz $NCH_2$-); 3.51 (t, 6.3 Hz, $NCH_2$-); 3.87 (s, OMe); 6.41 (d, 6.6 Hz); 6.57 (t, 7.5 Hz, H-5); 7.3 (d, 7.5 Hz); 7.81 (s, N=CH-). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: –6.3 (s, $Me_2Ga$); 54.8 (s, $NCH_2$); 56.0 (s, OMe); 56.3 (s, $NCH_2$); 115.7, 116.0, 117.6, 126.4 (aromatic quarternary signals could not be identified), 170.3 (CH=N).

*[N{Et₂GaO(C₆H₃OMe-3)CH=N–CH₂–CH₂-}₃]* (**2d**): To a benzene solution (25 mL) of triethylgallium etherate, (1.44 g, containing 2.93 mmol $Et_3Ga$), was added a solution of tris{(2-hydroxy-3-methoxy-benzylidene)aminoethyl}amine (537 mg, 0.98 mmol) with stirring which continued for 3 h. The solvent was evaporated under a reduced pressure to give a yellow solid (865 mg, 95%), m.p. 59 $^0$C. Anal. Calcd for $C_{42}H_{63}Ga_3N_4O_6$: C, 54.3; H, 6.8; N, 6.0; Ga, 22.5. Found: C, 54.4; H, 6.8; N, 6.0; Ga, 22.6%. IR in $cm^{-1}$: 1625 (νC=N); 520 (υ Ga–C). $^1H$ NMR ($CDCl_3$) δ: 0.46 (m, $GaCH_2$–, 12H); 1.05 (t, 7.8 Hz, $GaCH_2Me$, 18H); 2.89 (t, 6.9 Hz $NCH_2$–, 6H); 3.53 (t, 6.9 Hz, $NCH_2$–, 6H); 6.51–6.61 (m, H-5,6); 6.92 (d, 6.9 Hz, 3H); 7.92 (s, CH=N), 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 4.0 (s, $GaCH_2$); 9.8 (s, $GaCH_2Me$); 54.8 (s, $NCH_2$); 56.1 (s, OMe); 56.5 (s, $NCH_2$); 115.4, 115.6 (tert. carbon); 116.1 (tert. carbon); 116.3, 117.7 (tert. carbon); 126.4 (aromatic); 170.7 (s, CH=N).

*X-Ray crystallography:*

Intensity data on (**2a**) were collected at 298(2) K on a Rigaku AFC7S diffractometer fitted with Mo-Kα radiation so that $\theta_{max}$ = 27.5°. The structure was solved by direct methods and refinement[30] was on $F^2$, using data that had been corrected for absorption effects[31] with an empirical procedure with non hydrogen atoms modeled with anisotropic displacement parameter with hydrogen atoms in their calculated positions. Molecular structures were drawn using ORTEP.[32] Crystallographic data and data refinement details are given in Table 2.

**Table 2** Crystallographic and structural refinement data of **2a**

| Molecular formula | $C_{33}H_{45}Ga_3N_4O_3$ |
|---|---|
| Formula weight | 754.89 |
| Size (mm)/colour | 0.35 x 0.35 x 0.15/yellow |
| Crystal system | Trigonal |
| Space group | P -3 |
| *a*/Å | 17.2900 (8) |
| *b*/Å | 17.2900 (8) |
| *c*/Å | 14.175 (4) |
| *γ*/° | 120 |
| *V*/Å³ | 3669.9 (9) |
| *Z* | 4 |
| $d_{calc}$/g cm$^{-3}$ | 1.372 |
| μ (mm$^{-1}$)/F(000) | 2.222/1552 |
| θ for data collection/° | 2.72 to 27.51 |
| Limiting indices | $-22 \leq h \leq 19$<br>$0 \leq k \leq 22$<br>$-10 \leq l \leq 18$ |
| Absorption correction | Psi-scan |
| Refinement method | Full matrix least squares on $F^2$>0 |
| No. of unique reflns | 5620 |
| No. of obsd reflns with $I > 2\sigma(I)$ | 1408 |
| Data/restraints/parameters | 5535/0/260 |
| R_factor_gt/ wR_factor_gt | 0.0598/0.1378 |
| (R_factor_all/wR_Factor_ref | 0.2716/0.2530 |
| Goodness of fit in F² | 0.898 |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.462 and –0.463 |

We are grateful to Drs T. Mukherjee and D. Das for the encouragement of this work. CCDC 760549 contains the supplementary crystallographic data for [N{$Me_2GaO$-($C_6H_4$)CH=N–$CH_2$–$CH_2$-}$_3$]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK

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